# *Electronic Supporting Information*

# *for*

## Trio of nanoswitches in redox-potential controlled communication

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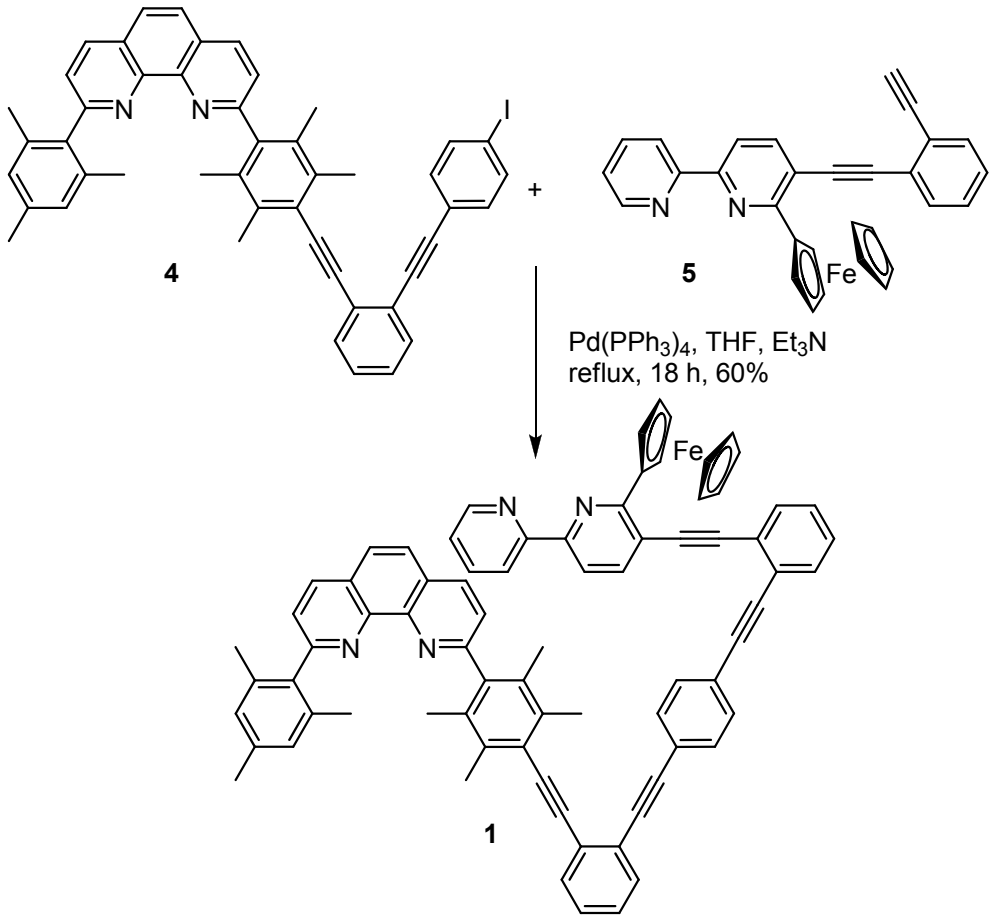
Abbreviations:
DCM: Dichloromethane
THF: Tetrahydrofuran
$Et_3N$: Triethylamine

## Synthesis

### General Information

All commercially available reagents were used directly without purification. Solvents used for column chromatography were distilled prior to use. Thin-layer chromatography was done using thin-layer chromatography plates (silica gel 60 F254, Merck). For column chromatography Silica gel 60 was used. Normal nuclear magnetic resonance (NMR) spectra were recorded on Bruker Avance 400 MHz spectrometer and kinetic study were performed on Varian 600 ASC using the deuterated solvent as the lock and the residual solvent as the internal reference. In $^{1}$H NMR assignments, the chemical shift (in ppm) is given first, followed, in brackets, by the multiplicity of the signal (s: singlet, d: doublet, t: triplet, dd: doublet of doublets, ddd: doublet of doublet of doublets, td: triplet of doublets, m: multiplet, bs: broad singlet), the value of the coupling constants in Hertz (Hz), the number of protons implied, and finally the assignment of the proton wherever possible. The numbering in the experimental section for the carbon atoms of the molecular formulae is only used for the assignments of the NMR signals and is not in accordance with IUPAC nomenclature rules. Anhydrous tetrahydrofuran (THF) was distilled over potassium. Triethyl amine and dichloromethane (DCM) were dried over calcium hydride. Melting points of solid compounds were measured on a Büchi (BÜCHI 510) melting point apparatus and remained uncorrected. IR spectra were recorded on a Perkin-Elmer FT-IR 1750. Electrospray ionisation mass spectra (ESI-MS) were recorded on a ThermoQuest LCQ Deca. Microanalyses were performed on a Euro elemental analyzer from EuroVector. Cyclic voltammetry (CV) measurements were conducted with a standard three-electrode set-up (1 mm Pt disk working electrode, a Pt auxiliary electrode and a silver wire as a pseudo-reference electrode) connected to a PARSTAT 2273 Advanced Electrochemical System. In all experiments, 0.1 M tetra-*n*-butylammonium hexafluorophosphate was used as supporting electrolyte and dry dichloromethane as solvent. All potentials are initially referenced to 2,4,6-triphenylpyryliumtetrafluoroborate (TPP) as internal standard, but are provided against SCE ($E_{TPP}^{0/+}$ = –0.38 V *vs* SCE).

## Synthetic scheme

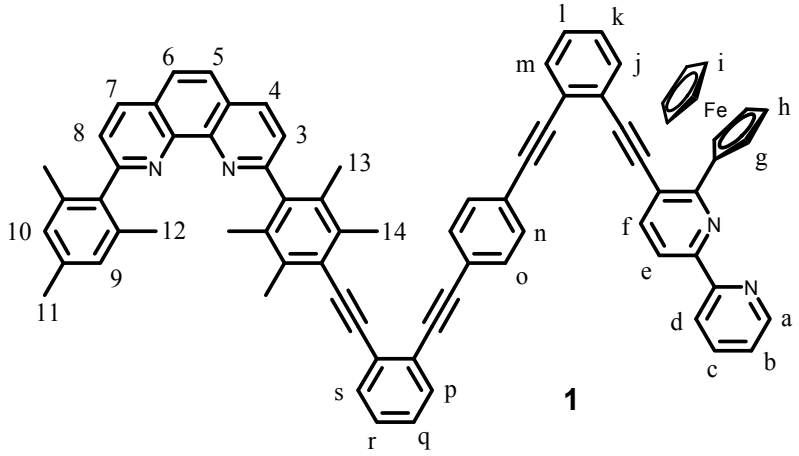



**Scheme S1**. Synthesis of switch **1**.

## Synthesis of nanoswitch 1

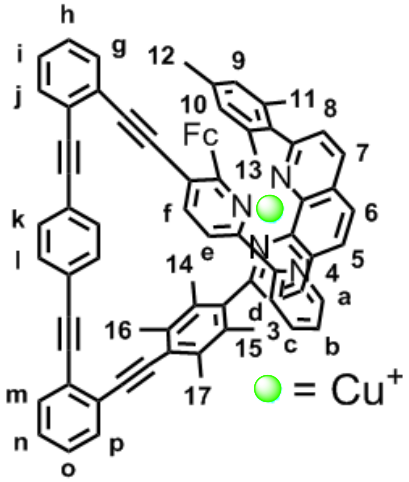
In a three-neck round bottom flask phenanthroline **4** (125 mg, 166 μmol) and bipyridine **5** (70.0 mg, 151 μmol) were loaded under argon atmosphere. 30 mL of dry THF and 30 mL of dry triethylamine were added to the flask and deaerated using a freeze-pump-thaw process trice. After addition of $Pd(PPh_3)_4$ (17.0 mg, 14.7 μmol), the reaction was heated to reflux for 18 h. The mixture was cooled and solvents were removed under vacuum. The residue was dissolved in DCM and extracted from water. The organic layer was dried over $Na_2SO_4$ and purified by chromatography over silica gel (15% EtOAc in hexane) to furnish ligand **1** as a reddish solid ($R_f$ = 0.3 in 20% EtOAc in hexane).

**Yield**: 60% (100 mg, 91 μmol). **Melting point:** 165 - 168 °C. **IR (KBr)**: $\tilde{\nu}$ = 3052, 2993, 2916, 2862, 2280, 2200, 1950, 1922, 1810, 1697, 1600, 1582, 1540, 1500, 1479, 1436, 1385, 1350, 1265, 1214, 1166, 1139, 1095, 1012, 952, 842, 756, 627, 585 $cm^{-1}$. **$^1$H NMR (400 MHz, $CD_2Cl_2$):** $\delta$ = 1.91 (s, 6 H, 13-H), 2.03 (s, 6 H, 12-H), 2.32 (s, 3 H, 11-H), 2.56 (s, 6 H, 14-H), 4.06 (s, 5 H, i-H), 4.32 (t, $^3J$ = 2.0 Hz, 2 H, h-H), 5.57 (t, $^3J$ = 2.0 Hz, 2 H, g-H), 6.95 (s, 2 H, 9-, 10-H), 7.21 (ddd, $^3J$ = 8.0 Hz, $^3J$ = 4.8 Hz, $^4J$ = 1.2 Hz, 1 H, b-H), 7.33-7.39 (m, 2 H, k-, l-H), 7.40-7.46 (m, 2 H, q-, r-H), 7.52 (d, $^3J$ = 8.0 Hz, 1 H, 8-H), 7.54 (s, 4 H, n-, o-H), 7.56 (d, $^3J$ = 8.0 Hz, 1 H, 3-H), 7.61-7.67 (m, 3 H, j-, m-, p-H), 7.70-7.72 (m, 1 H, s-H), 7.78 (td, $^3J$ = 8.0 Hz, $^4J$ = 1.2 Hz, 1 H, c-H), 7.90 (s, 2 H, 5-, 6-H), 7.95 (d, $^3J$ = 8.4 Hz, 1 H, f-H), 8.23 (d, $^3J$ = 8.4 Hz, 1 H, e-H), 8.32 (d, $^3J$ = 8.0 Hz, 1 H, 7-H), 8.33 (d, $^3J$ = 8.0 Hz, 1 H, 4-H), 8.54 (dt, $^3J$ = 8.0 Hz, $^4J$ = 1.2 Hz, $^5J$ = 1.2 Hz, 1 H, d-H), 8.68 (ddd, $^3J$ = 4.8 Hz, $^4J$ = 1.2 Hz, $^5J$ = 1.2 Hz, 1 H, a-H) ppm. **$^{13}$C NMR (100 MHz, $CD_2Cl_2$)**: $\delta$ = 17.7, 18.7, 20.4, 21.2, 70.0, 70.1, 70.3, 84.0, 90.4, 91.0, 92.9, 93.2, 93.5, 93.6, 95.0, 95.8, 115.9, 117.0, 121.4, 123.0, 123.2, 123.7, 124.1, 124.7, 124.9, 124.9, 125.6, 125.9, 126.4, 126.6, 126.7, 127.5, 127.6, 128.1, 128.5, 128.7, 128.8, 128.8, 132.0, 132.1, 132.1, 132.2, 132.4, 132.6, 132.7, 136.0, 136.3, 136.4, 136.7, 137.0, 137.7, 138.4, 142.1, 142.8, 146.6, 146.6, 149.4, 154.6, 156.0, 159.1, 160.5, 161.3 ppm. **ESI-MS:** *m/z* (%) = 1093.4 (100) [**1**•H]$^+$; calcd. *m/z* = 1093.6. **Elemental analysis** $C_{77}H_{56}FeN_4$•0.5 $CH_3COOEt$; Calcd: C, 83.59; H, 5.15; N, 4.94; Found: C, 83.27; H, 5.17; N, 5.00.




**1**

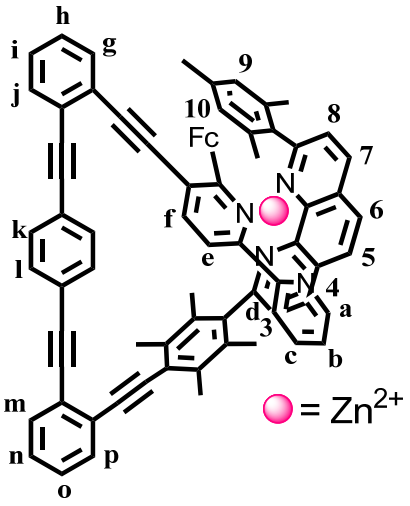
**Synthesis of [Cu(1)]$^+$**




Switch **1** (770 µg, 704 µmol) and $[Cu(CH_3CN)_4]B(C_6F_5)_4$ (638 µg, 704 µmol) were placed in an NMR tube. To this mixture, $CD_2Cl_2$ was added and subsequently NMR was recorded.

**Yield**: quantitative. **$^1$H NMR (400 MHz, $CD_2Cl_2$):** $\delta$ = 1.53 (s, 3 H, duMe-H), 1.65 (s, 3 H, mesMe-H), 1.73 (s, 3 H, duMe-H), 1.78 (s, 3 H, mesMe-H), 1.68 (s, 3 H, duMe-H), 1.97 (s, 3 H, mesMe-H), 2.17 (s, 3 H, duMe-H), 3.32 (bs, 1 H, Fc-H), 3.67 (bs, 1 H, Fc-H), 3.89 (bs, 5 H, Fc-H), 4.54 (bs, 1 H, Fc-H), 4.92 (bs, 1 H, Fc-H), 6.35 (s, 1 H, 9/10-H), 6.43 (s, 1 H, 10/9-H), 7.29 (d, $^3J$ = 8.4 Hz, 1 H, e-H), 7.31 (ddd, $^3J$ = 8.0 Hz, $^3J$ = 4.8 Hz, $^4J$ = 1.2 Hz, 1 H, b-H), 7.40-7.42 (m, 2 H, h-, i-H), 7.46-7.48 (m, 2 H, n-, o-H), 7.51 (s, 4 H, k-, l-H), 7.60-7.64 (m, 3 H, g-, j-, f-H), 7.66-7.72 (m, 3 H, d-, m-, p-H), 7.77 (d, $^3J$ = 8.4 Hz, 2 H, 3-, 8-H), 7.80 (td, $^3J$ = 8.0 Hz, $^4J$ = 1.2 Hz, 1 H, c-H), 8.03 (dd, $^3J$ = 4.8 Hz, $^4J$ = 1.2 Hz, 1 H, a-H), 8.19 (s, 2 H, 5-, 6-H), 8.63 (d, $^3J$ = 8.0 Hz, 1 H, 4/7-H), 8.65 (d, $^3J$ = 8.0 Hz, 1 H, 7/4-H) ppm. **ESI-MS:** *m/z* (%) = 1155.3 (100) $[Cu(\mathbf{1})]^+$; calcd. *m/z* = 1155.5.

**Synthesis of $[Zn(1)]^{2+}$**




$Zn(OTf)_2$ (204 µg, 562 µmol) was placed in an NMR tube and $CD_3CN$ (200 µL) was added to dissolve it. Thereafter, switch **1** (613 µg, 562 µmol) and $CD_2Cl_2$ (600 µL) were added. Subsequently, the $^1H$ NMR was measured without purification.

**Yield**: quantitative. **$^1H$ NMR (400 MHz, $CD_2Cl_2$:$CD_3CN$ (3:1)):** $\delta$ = 1.53 (s, 3 H, mesMe-H), 1.71 (s, 3 H, duMe-H), 1.83 (s, 3 H, mesMe-H), 1.86 (s, 6 H, duMe-H), 1.89 (s, 3 H, duMe-H), 2.22 (s, 3 H, mesMe-H), 3.35 (td, $^3J$ = 2.8 Hz, $^4J$ = 1.2 Hz, 1 H, Fc-H), 3.84 (ddd, $^3J$ = 2.8 Hz, $^4J$ = 1.2 Hz, $^5J$ = 0.4 Hz, 1 H, Fc-H), 3.98 (s, 5 H, Fc-H), 4.37 (td, $^3J$ = 2.8 Hz, $^4J$ = 1.2 Hz, 1 H, Fc-H), 5.48 (ddd, $^3J$ = 2.8 Hz, $^4J$ = 1.2 Hz, $^5J$ = 0.4 Hz, 1 H, Fc-H), 6.03 (s, 1 H, 9/10-H), 6.43 (s, 1 H, 10/9-H), 7.44-7.46 (m, 2 H, n-, o-H), 7.54-7.56 (m, 2 H, h-, i-H), 7.58 (d, $^3J$ = 8.4 Hz, 1 H, e-H), 7.62 (s, 4 H, k-, l-H), 7.63-7.67 (m, 3 H, g-, j-, m-H), 7.74 (ddd, $^3J$ = 8.0 Hz, $^3J$ = 5.2 Hz, $^4J$ = 1.2 Hz, 1 H, b-H), 7.81-7.83 (m, 1 H, p-H), 7.89 (d, $^3J$ = 8.4 Hz, 1 H, f-H), 7.93 (d, $^3J$ = 8.4 Hz, 1 H, 3/8-H), 8.02 (d, $^3J$ = 8.0 Hz, 1 H, d-H), 8.17 (d, $^3J$ = 8.4 Hz, 1 H, 8/3-H), 8.20 (td, $^3J$ = 8.0 Hz, $^4J$ = 1.2 Hz, 1 H, c-H), 8.39 (d, $^3J$ = 8.8 Hz, 1 H, 5/6-H), 8.45 (d, $^3J$ = 8.8 Hz, 1 H, 6/5-H), 8.71 (d, $^3J$ = 5.2 Hz, 1 H, a-H), 8.92 (d, $^3J$ = 8.4 Hz, 1 H, 4/7-H), 9.12 (d, $^3J$ = 8.4 Hz, 1 H, 7/4-H) ppm. **ESI-MS:** *m/z* (%) = 578.2 (100) $[Zn(\mathbf{1})]^{2+}$; calcd. *m/z* = 578.6.

## Characterisation by spectra

### Characterisation of ligand 1

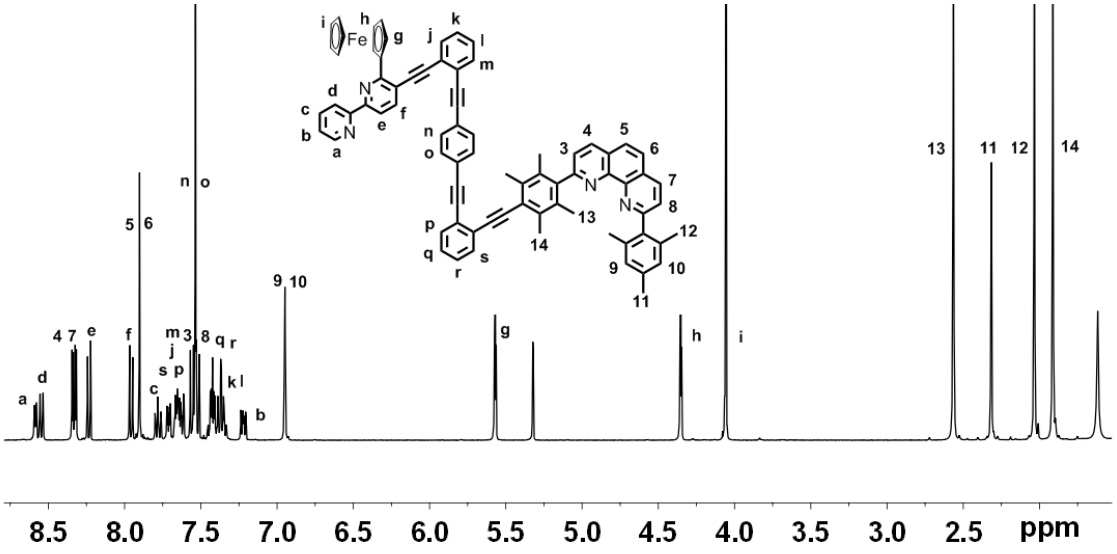



**Figure S1.** $^{1}$H NMR spectrum (400 MHz, $CD_2Cl_2$, 298 K) of compound **1**.

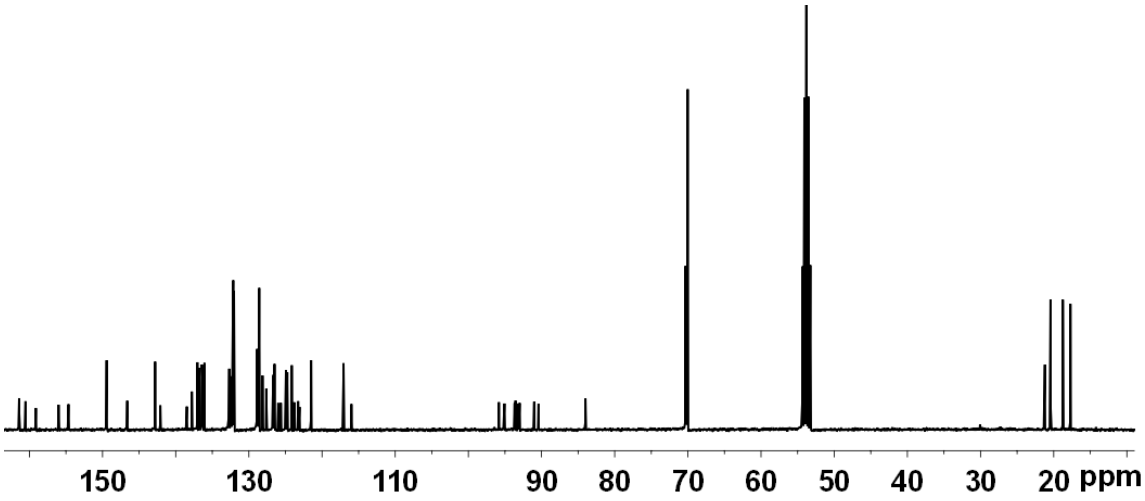



**Figure S2.** $^{13}$C NMR spectrum (100 MHz, $CD_2Cl_2$, 298 K) of compound **1**.

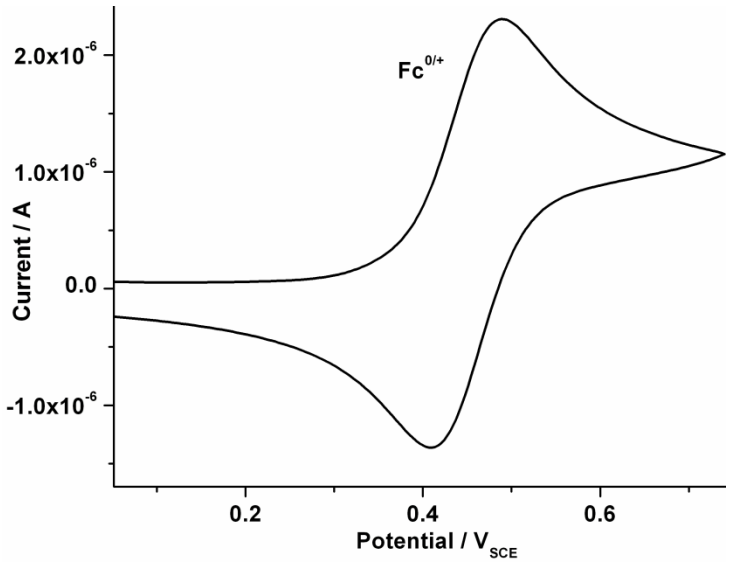



**Figure S3.** CV of switch **1**. $E_{1/2}$ = 450 $mV_{SCE}$ in dry dichloromethane at a scan rate of 100 mV $s^{-1}$.

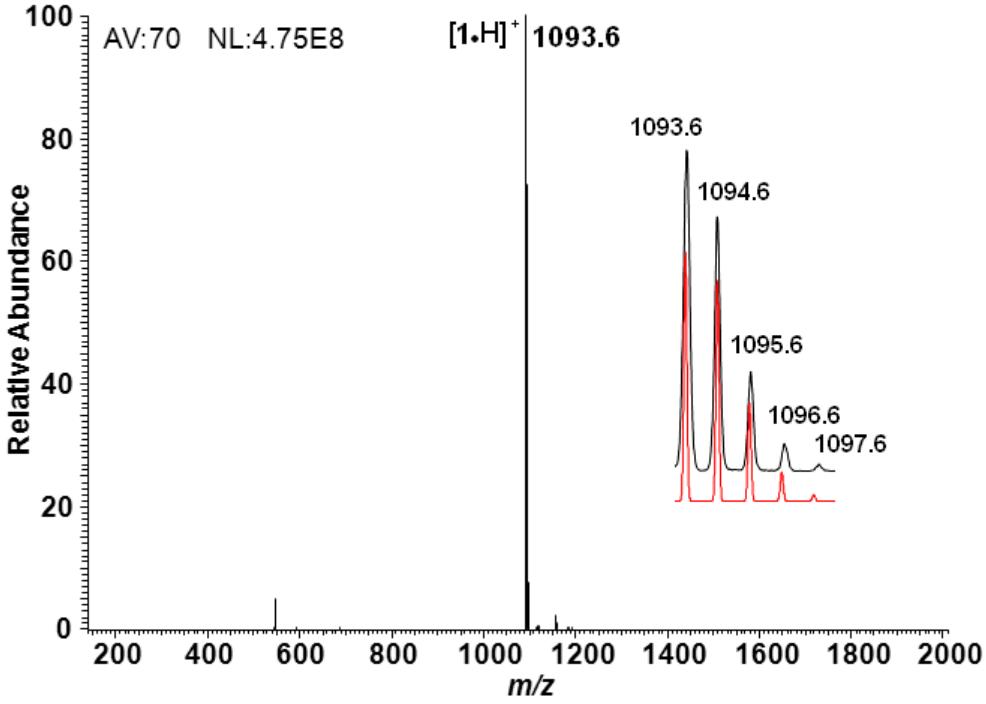



**Figure S4.** ESI-MS spectrum of switch $[\mathbf{1}\bullet H]^+$ in $CH_2Cl_2$.

## Characterisation of complexes

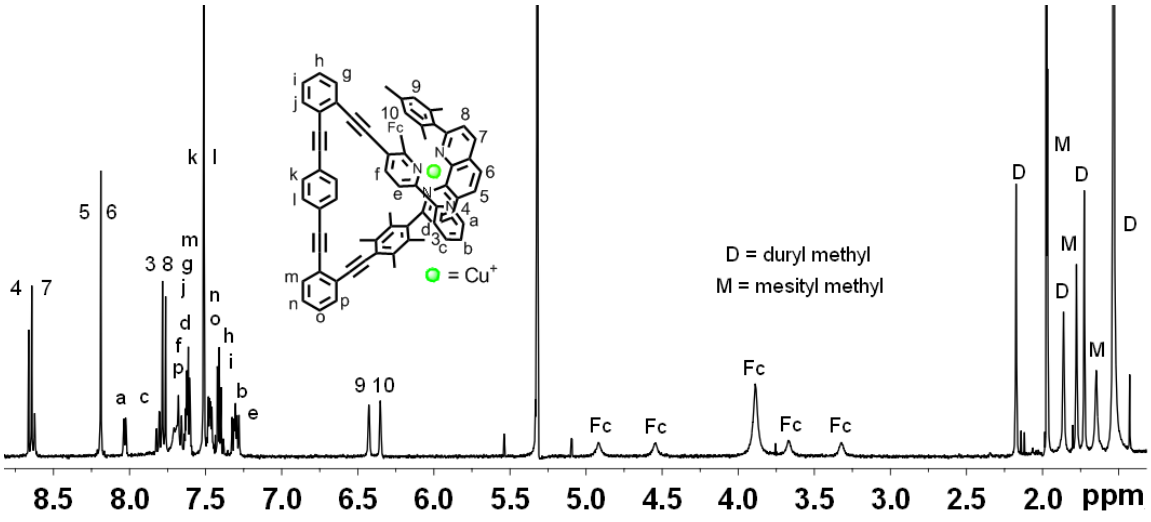



**Figure S5.** $^{1}$H NMR spectrum (400 MHz, $CD_2Cl_2$, 298 K) of complex [Cu(**1**)]$^{+}$.

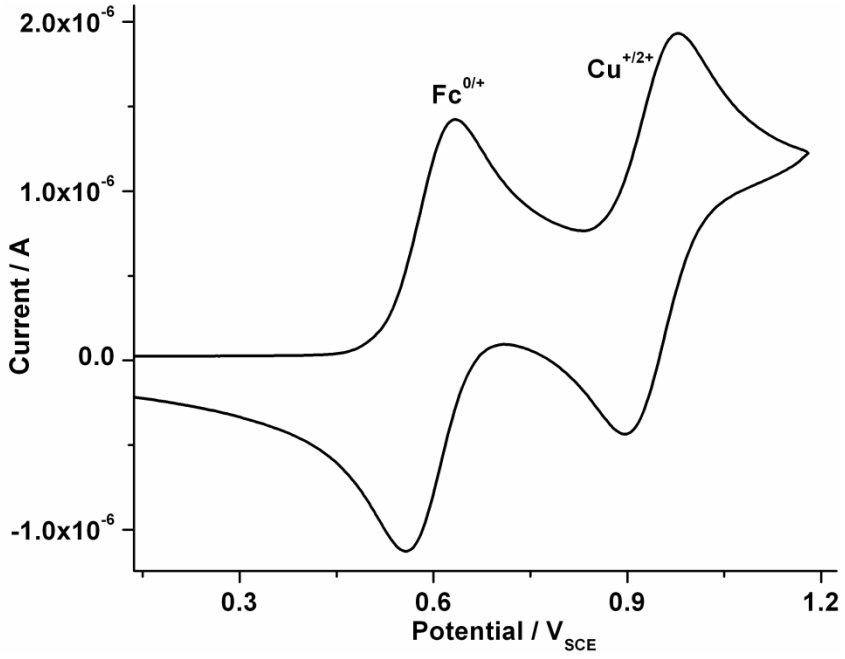



**Figure S6.** CV of complex [Cu(**1**)]$^{+}$. $E_{1/2}{}^{Fc^{0/+}}$ = 610 $mV_{SCE}$ and $E_{1/2}{}^{Cu^{+/2+}}$ = 940 $mV_{SCE}$ in dry dichloromethane at a scan rate of 100 mV $s^{-1}$.

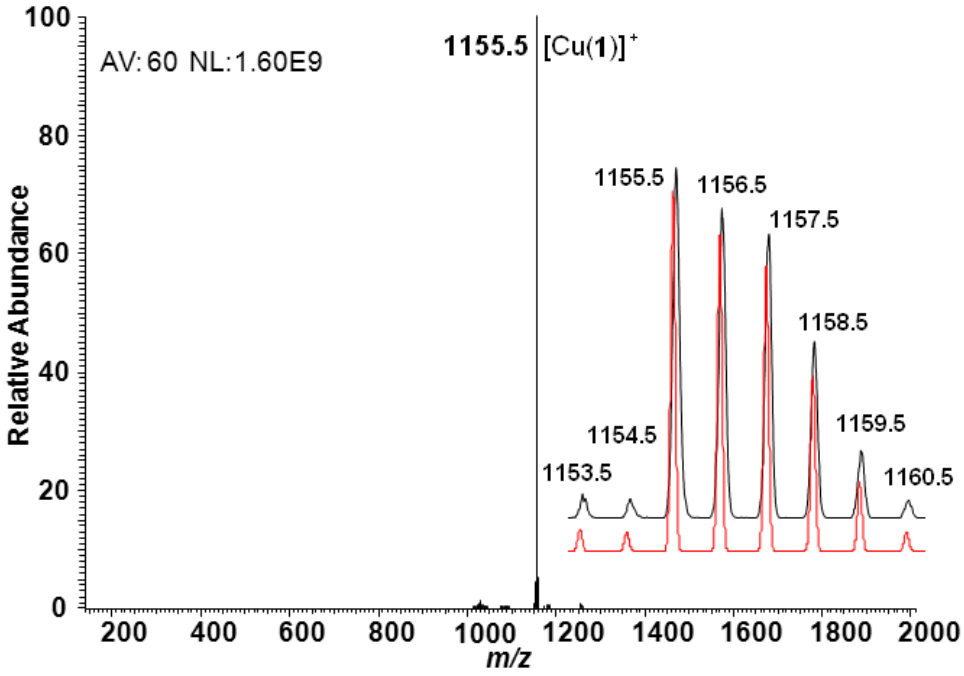



**Figure S7.** ESI-MS spectrum of complex $[Cu(\mathbf{1})]^{+}$ in $CD_2Cl_2$.

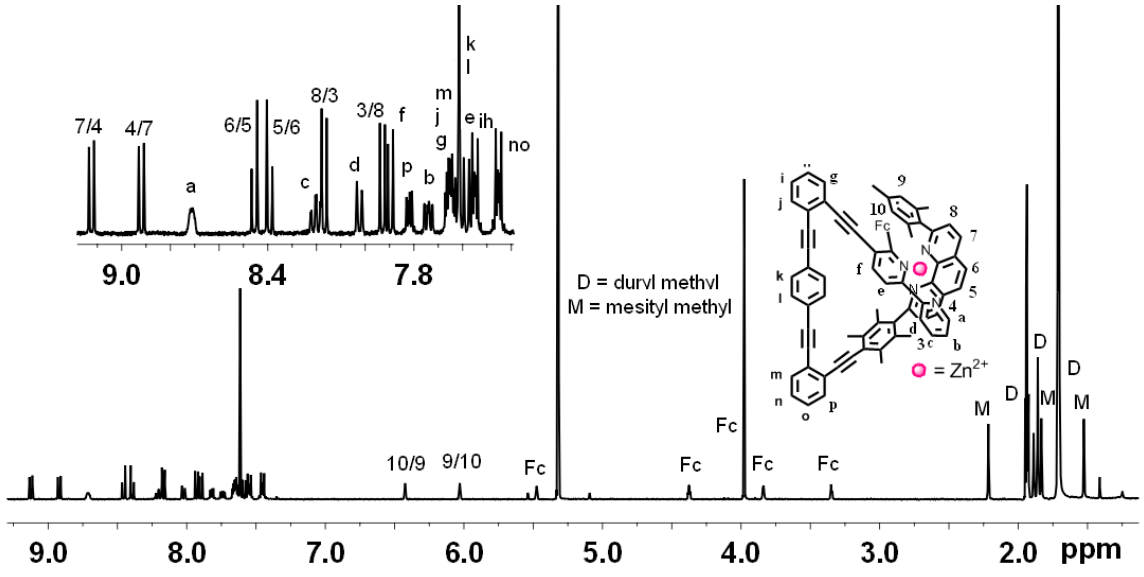



**Figure S8.** $^{1}H$ NMR spectrum (400 MHz, $CD_2Cl_2$, 298 K) of complex $[Zn(\mathbf{1})]^{2+}$.

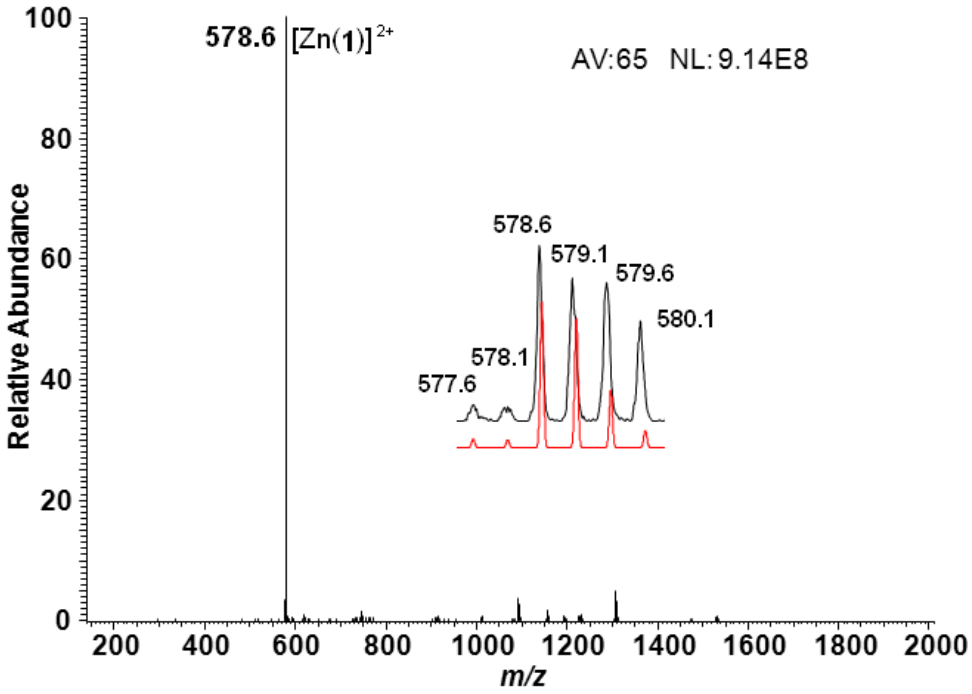



**Figure S9:** ESI-MS spectrum of complex $[Zn(\mathbf{1})]^{2+}$ in $CH_2Cl_2$.

## Communication between two nanoswitches

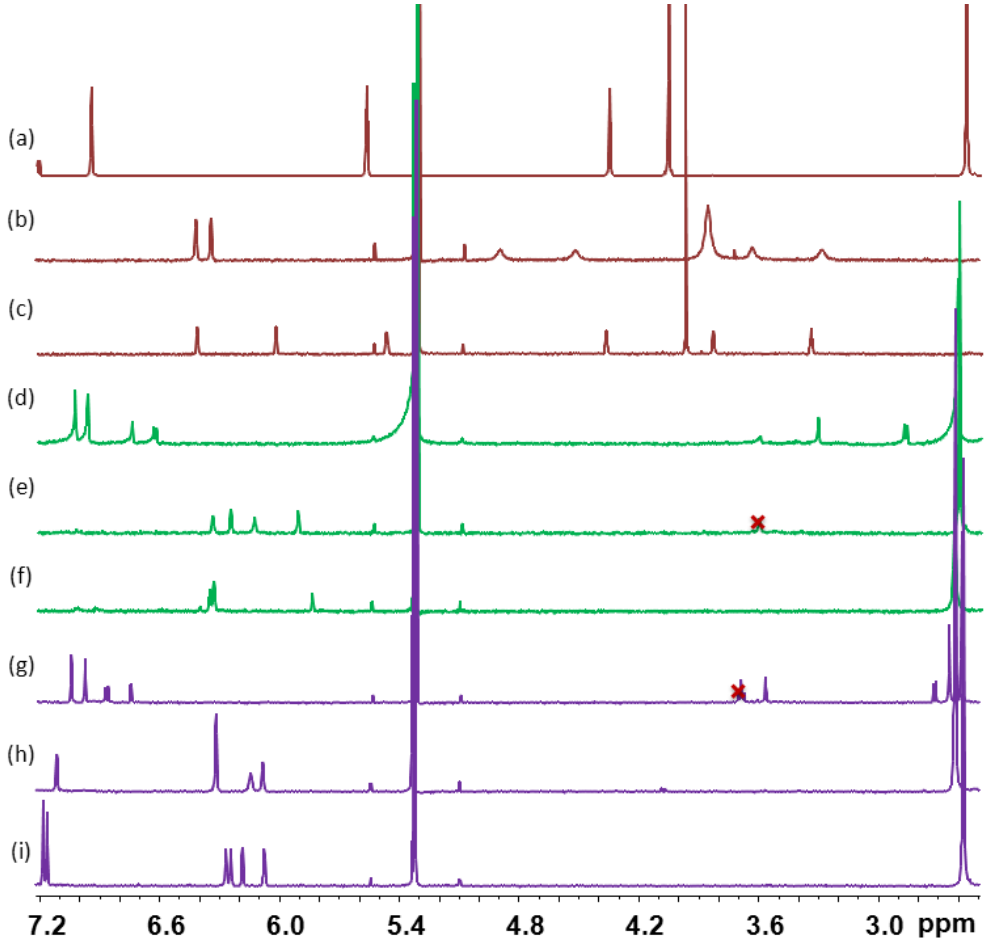



**Figure S10.** Partial $^{1}$H NMR spectra (400 MHz, $CD_2Cl_2$, 298 K) of switches and their complexes. The different NMR traces represent: (a) switch **1**; (b) [Cu(**1**)]$^{+}$; (c) [Zn(**1**)]$^{2+}$; (d) switch **2**; (e) [Cu(**2**)]$^{+}$; (f) [Zn(**2**)]$^{2+}$; (g) switch **3**; (h) [Cu(**3**)]$^{+}$; (i) [Zn(**3**)]$^{2+}$.

## $Cu^+$ translocation

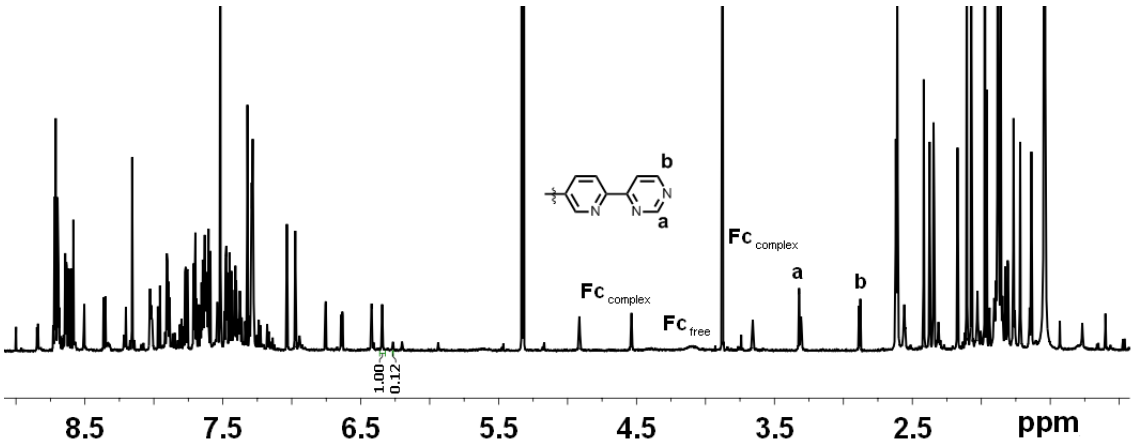



**Figure S11.** $^1$H NMR spectrum (400 MHz, $CD_2Cl_2$, 298 K) of the mixture when switch **1** was added to [Cu(**2**)]$B(C_6F_5)_4$ (2.70 mM). The spectrum shows a 90 : 10 ratio of $[Cu(\mathbf{1})]^+$ and $[Cu(\mathbf{2})]^+$.

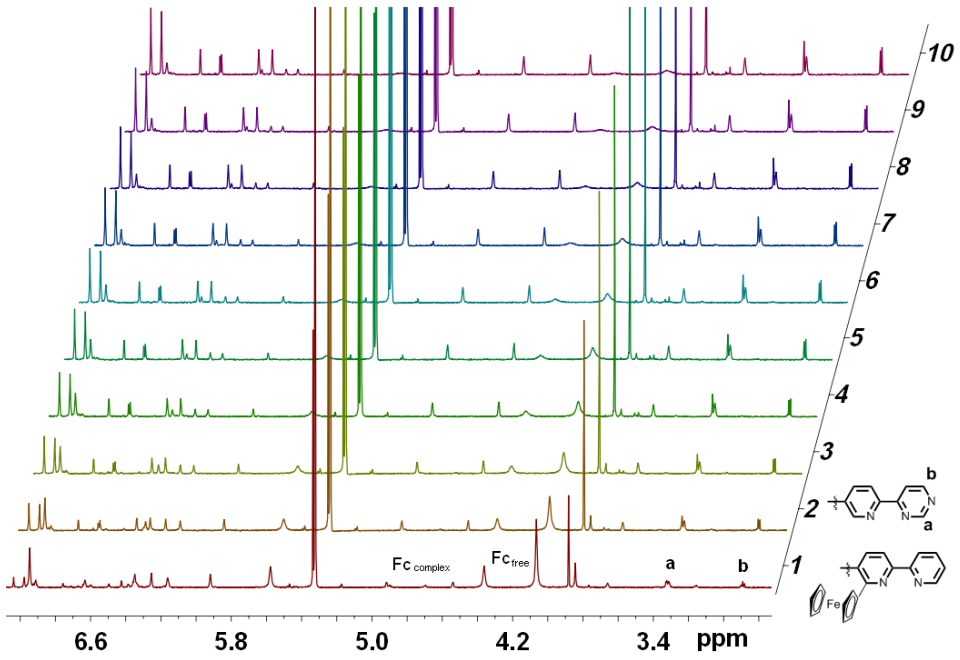



**Figure S12.** $^1$H NMR spectrum (600 MHz, $CD_2Cl_2$) of the $Cu^+$ translocation at 298 K (2.70 mM). To a solution of [Cu(**2**)]$B(C_6F_5)_4$ (1.41 mg, 0.570 µmol) in $CD_2Cl_2$ in an NMR tube was added switch **1** (0.623 mg, 0.570 µmol) as a solid. Subsequently, $^1$H NMR spectra were recorded. The NMR traces represent: (from bottom) the spectrum recorded after 8 min of mixing and thereafter spectra recorded in 10 min intervals. After 58 min full equilibration was reached showing a 90:10 ratio of $[Cu(\mathbf{1})]^+$ and $[Cu(\mathbf{2})]^+$.

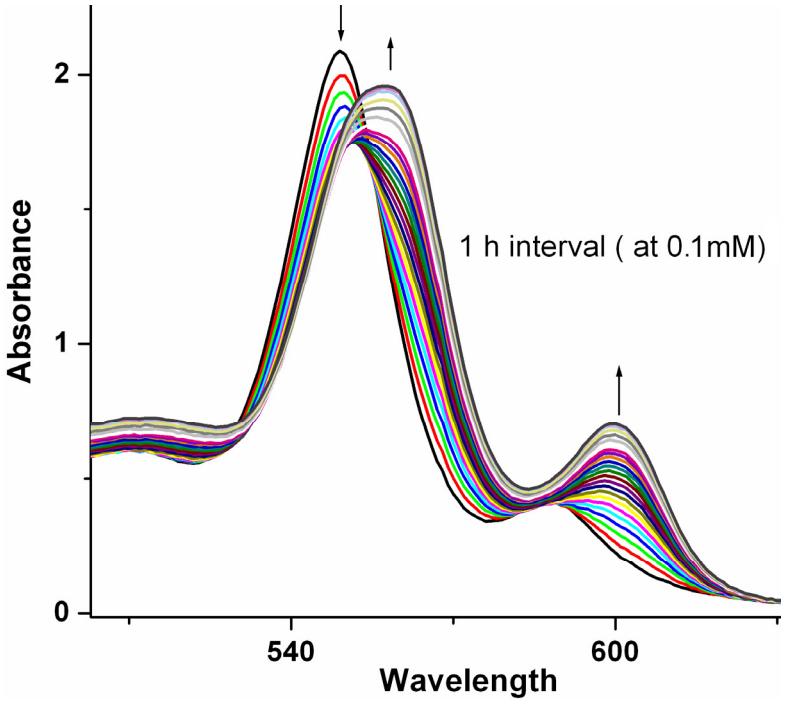



**Figure S13.** UV-Vis spectra of the $Cu^{+}$ translocation between switches **1** and **2**. A stock solution at $c = 10^{-4}$ M of [Cu(**2**)]$B(C_6F_5)_4$ was prepared, from which 2 mL were put into a 1 cm cuvette. Subsequently, switch **1** (220 µg, 201 µmol) was added as a solid to the solution. Then within a minute, measurements were started and recorded at 1 h intervals. The translocation reached the final equilibrium after 26 h.

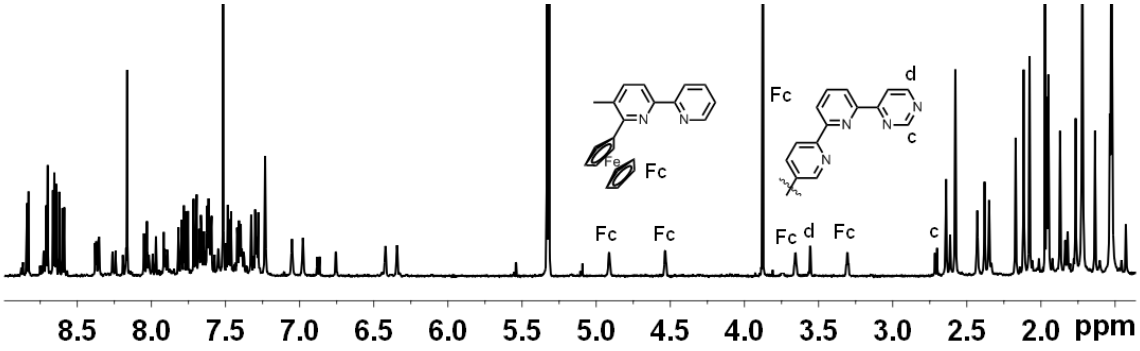



**Figure S14.** $^{1}H$ NMR spectrum (400 MHz, 298 K) of the mixture when switch **1** (0.563 mg, 0.515 µmol) was added to [Cu(**3**)]$B(C_6F_5)_4$ (1.32 mg, 0.515 µmol) in $CD_2Cl_2$ (0.64 mM). The spectrum shows only presence of $[Cu(\mathbf{1})]^{+}$ and the free switch **3** and thus complete translocation of $Cu^{+}$ ions.

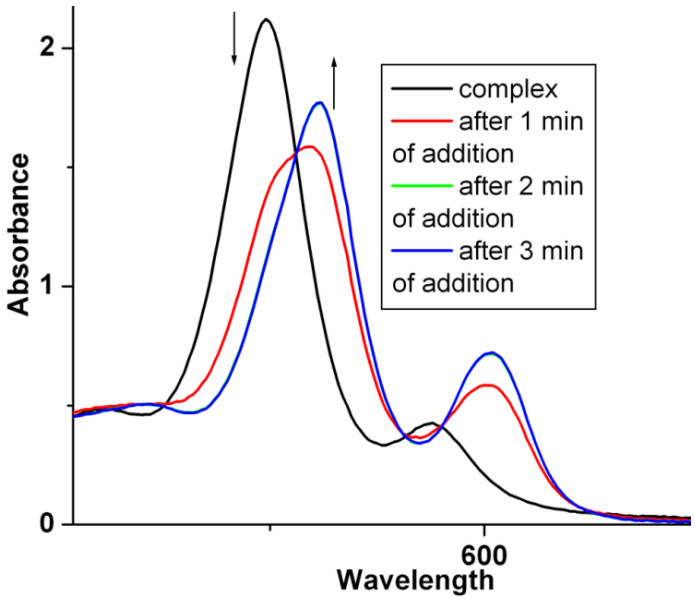



**Figure S15.** UV-Vis spectra of the $Cu^{+}$ translocation between switches **1** and **3**. A stock solution at $c = 10^{-4}$ M of $[Cu(\mathbf{3})]B(C_6F_5)_4$ was taken (2 mL) into a 1 cm cuvette, then switch **1** (220 μg, 201 μmol) was added as a solid to the solution. Then within a minute, measurements were started and recorded at time intervals of 1 min. Translocation was completed 3 min after mixing.

## $Zn^{2+}$ translocation

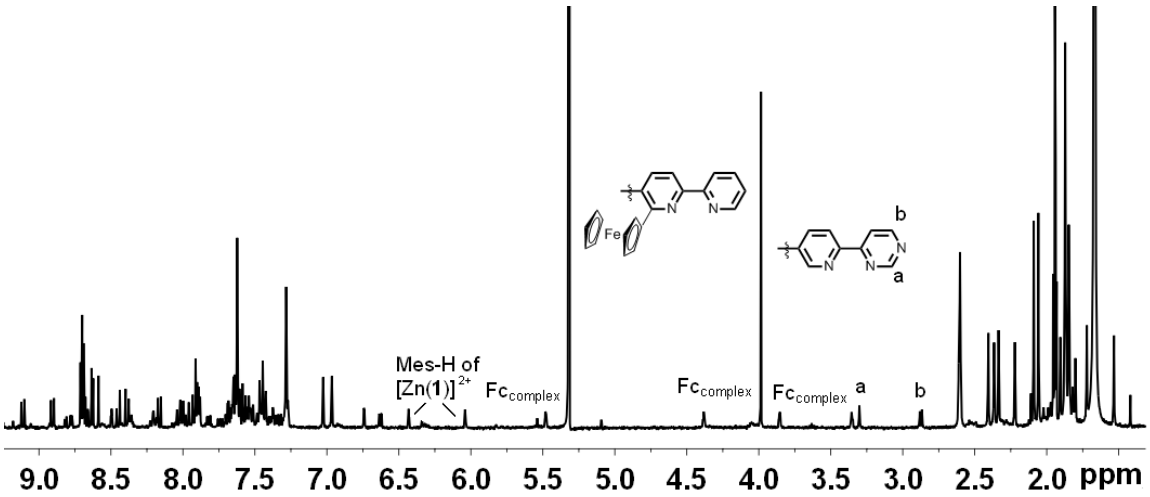



**Figure S16.** $^{1}H$ NMR spectrum (400 MHz, 298 K) obtained after addition of switch **1** (0.611 mg, 0.558 μmol) to $[Zn(\mathbf{2})](OTf)_2$ (1.17 mg, 0.558 μmol) in $CD_2Cl_2$ (0.70 mM). The spectrum demonstrates complete translocation of the $Zn^{2+}$ ions to afford $[Zn(\mathbf{1})]^{2+}$ and free switch **2**.

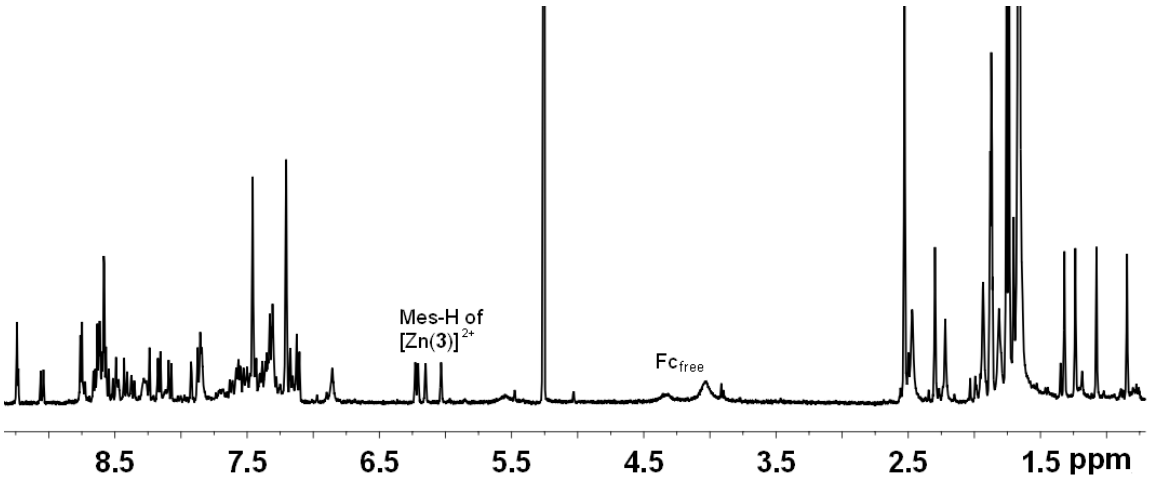



**Figure S17.** $^1$H NMR spectrum (400 MHz, $CD_2Cl_2$, 298 K) after adding switch **3** (1.020 mg, 0.562 μmol) to [Zn(**1**)](OTf)$_2$ (0.817 mg, 0.562 μmol) (0.70 mM). The spectrum demonstrates complete translocation of the $Zn^{2+}$ ions to afford [Zn(**3**)]$^{2+}$ and free switch **1**.

## Reversible communications between switches 1 and 2

### Analysis by $^1$H-NMR

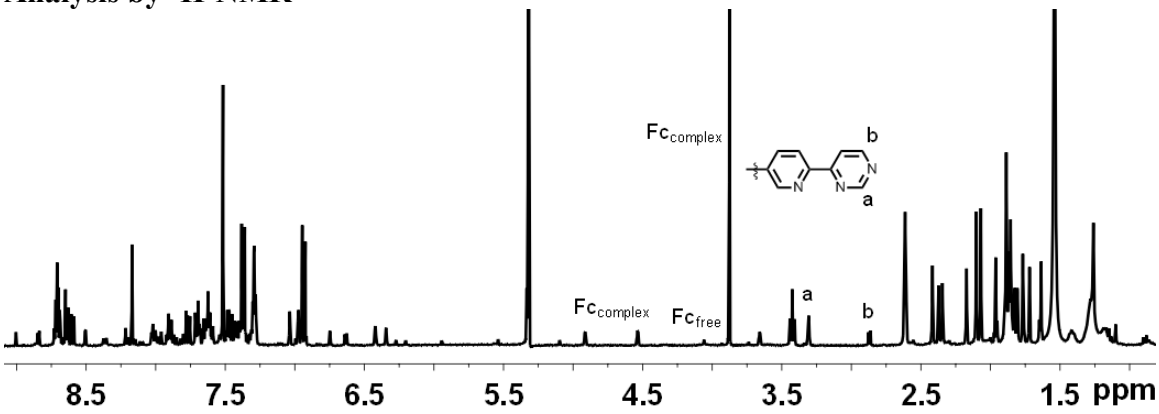



**Figure S18.** $^1$H NMR (400 MHz, $CD_2Cl_2$, 298 K) after the reduction of the mixture containing **1**$^+$ and [Cu(**2**)]$^+$. A mixture of **1** (487 μg, 457 μmol), **2** (774 μg, 457 μmol) and [Cu(CH$_3$CN)$_4$]B(C$_6$F$_4$)$_5$ (416 μg, 457 μmol) was placed in an NMR tube and dissolved in $CD_2Cl_2$. The solution was then treated with tris(4-bromophenyl)aminium tetrafluoroborate[1] (260 μg, 457 μmol). The colour of the solution turned from greenish pink, indicative of the intramolecularly coordinated zinc porphyrin of switch **2**, to reddish pink attesting free zinc porphyrin and formation of [Cu(**2**)]$^+$ after heating the solution in a water bath at 40 °C for a few minutes to assure complete translocation. The putative solution was finally reduced with 3-(11-bromoundecyl)-1,1´-biferrocenylene (**BFD**) (274 μg, 457 μmol). The NMR spectrum recorded thereafter shows the same results (90:10) as observed without oxidation-reduction step.

**Analysis by UV-vis**

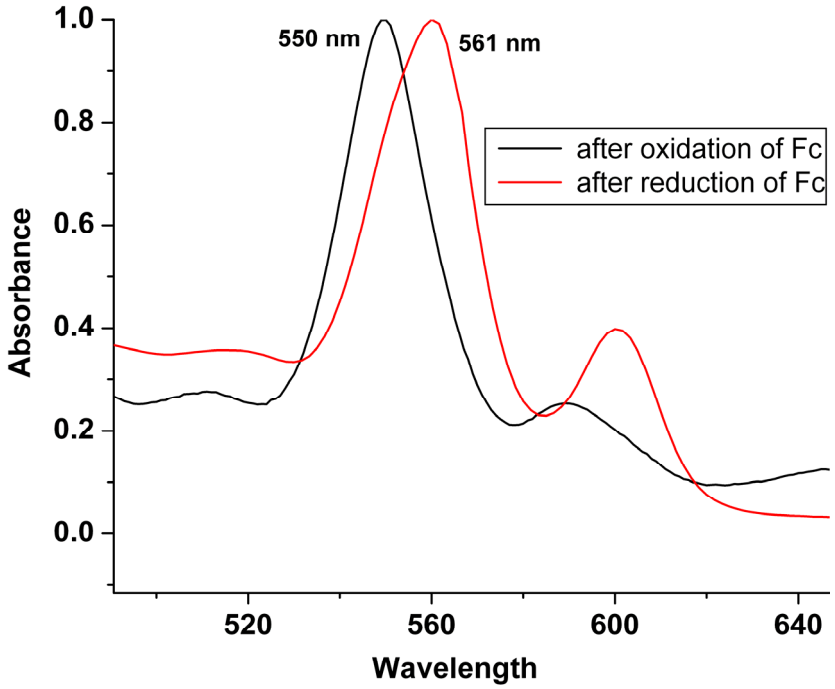



**Figure S19.** Normalised UV-vis spectra showing the reversible copper ion translocation between **1** and **2**. A solution ($10^{-4}$ M) consisting of **1**, **2** and $[Cu(CH_3CN)_4]B(C_6F_5)_4$ in dry DCM was treated with solid tris(4-bromophenyl)aminium hexachloroantimonate (**TBPA**$^{+\bullet}$ $SbCl_6^-$) (0.163 mg, 0.200 µmol), then UV-Vis spectra were collected at time intervals of 1 min. The black trace shows full translocation of copper ions from switch **1** to switch **2** within 4 min after ferrocene oxidation as detected from the reorganisation of the switching arm from the zinc porphyrin to the phenanthroline station (se the absorbance changes from 561 to 550 nm). The red trace represents the reverse copper ion translocation from switch **2** to switch **1** after reduction of ferrocene with solid **dmfc** (0.065 mg, 0.20 µmol) with the absorption changing from 550 to 561 nm. The process was completed after 18 h.

**Analysis by ESI-MS**

A solution of $[Cu(\mathbf{1})]B(C_6F_5)_4$ (296 µg, 161 µmol) and **2** (280 µg, 161 µmol) in dry DCM was treated with **TBPA**$^{+\bullet}SbCl_6^-$ (131 µg, 161 µmol). The solution was then divided into two parts. The first part was analysed by ESI-MS (Figure S20) and the second part was reacted with **dmfc** (26 µg, 81 µmol) and, finally, monitored with ESI-MS (Figure S21).

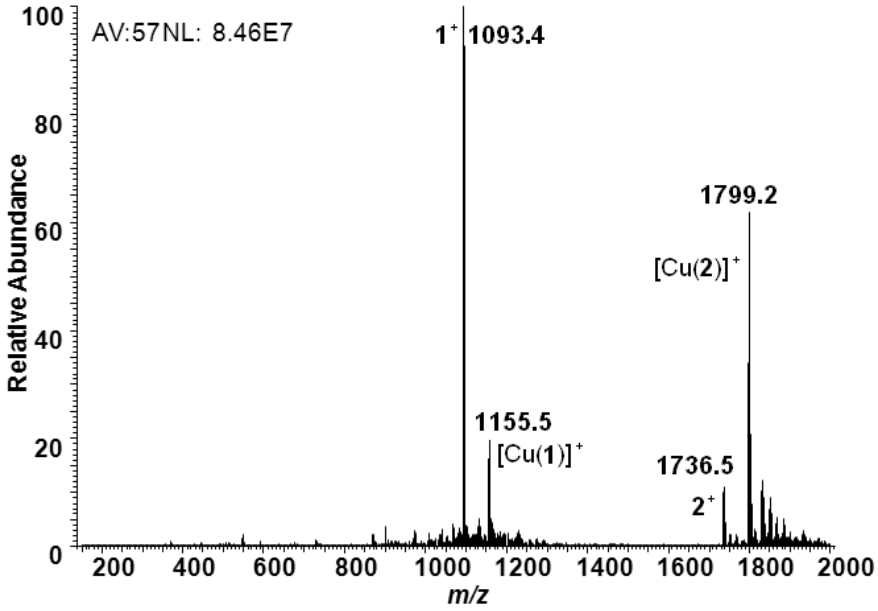



**Figure S20.** ESI-MS spectrum after oxidation of a mixture of $[Cu(\mathbf{1})]^+$ and **2** with one equiv. of tris(4-bromophenyl)aminium hexachloroantimonate (131 μg, 161 μmol) in dichloromethane.

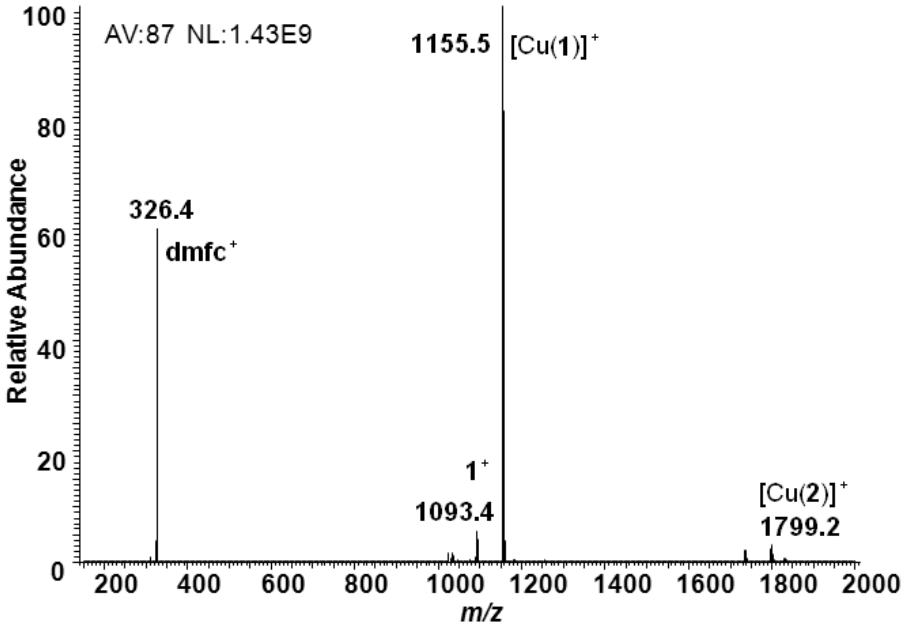



**Figure S21.** ESI-MS spectrum obtained after reduction of the above solution (Figure S20) with decamethylferrocene (**dmfc**) (26 μg, 81 μmol).

## Reversible communications between switches 1 and 3

### Analysis by $^{1}$H-NMR

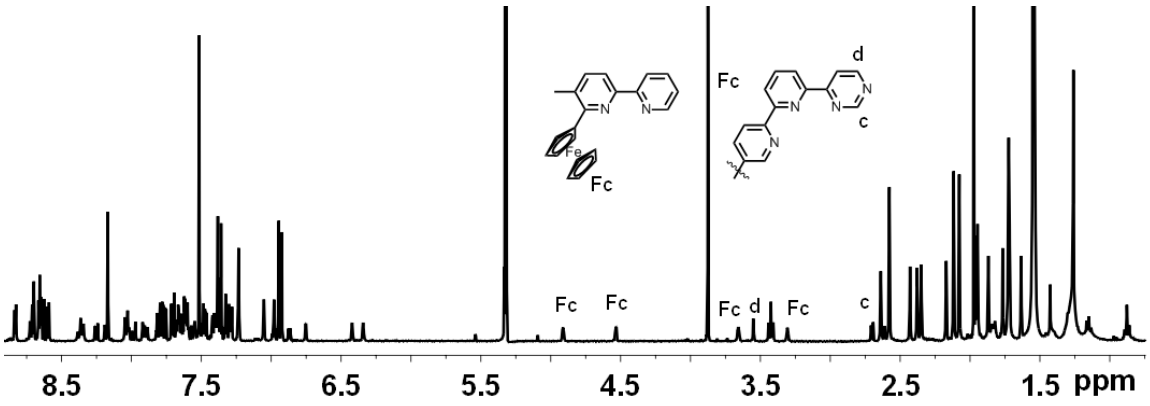



**Figure S22.** $^{1}$H NMR (400 MHz, $CD_2Cl_2$, 298 K) after reverse translocation of $Cu^{+}$ between switches **1** and **3**. In an NMR tube a mixture of **1** (464 µg, 425 µmol), **3** (770 µg, 425 µmol) and $[Cu(CH_3CN)_4]B(C_6F_4)_5$ (385 µg, 425 µmol) was taken in $CD_2Cl_2$. The solution was then treated with tris(4-bromophenyl)aminium tetrafluoroborate (242 µg, 425 µmol). After heating the solution in a water bath at 40 °C for a few minutes to assure complete translocation, a colour change occurred from a greenish pink suggesting a co-ordinated zinc porphyrin (of free switch **3**) to a reddish pink attesting a uncoordinated porphyrin and thus formation of $[Cu(\mathbf{3})]^{+}$. The putative solution was finally reacted with 3-(11-bromoundecyl)-1,1´-biferrocenylene (**BFD**) (255 µg, 425 µmol), then a NMR was recorded. The spectrum demonstrated complete reverse translocation of $Cu^{+}$ to furnish switch $[Cu(\mathbf{1})]^{+}$.

**Analysis by UV-Vis**

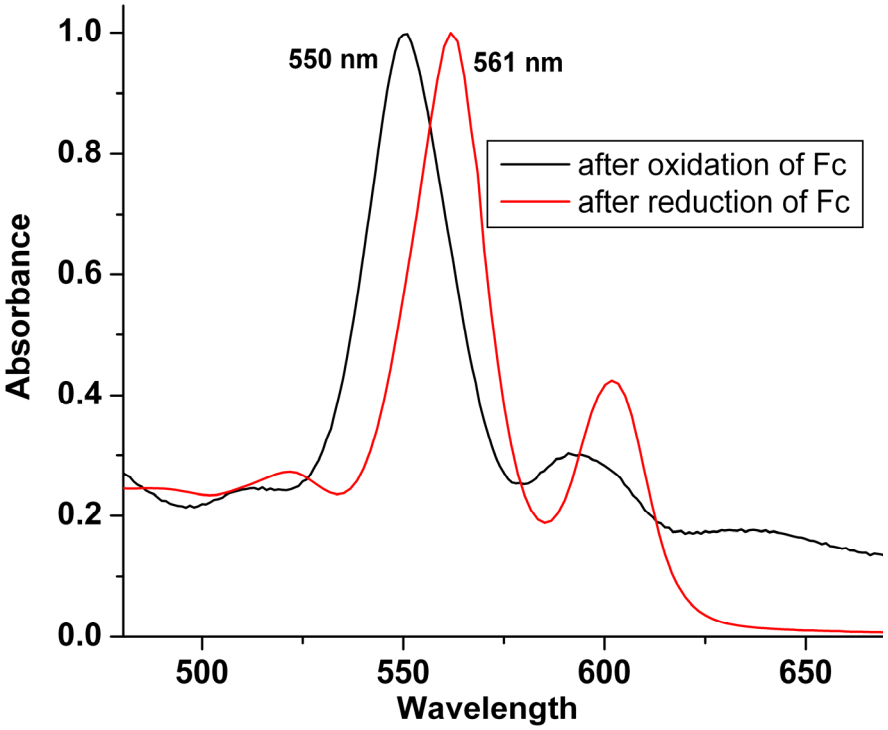



**Figure S23.** Normalised UV-Vis spectra showing reversible copper ion translocation between switches **1** and **3**. A solution containing $[Cu(\mathbf{1})]^+$ and switch **3** (1:1) at $10^{-4}$ M was treated with solid tris(4-bromophenyl)aminium hexachloroantimonate (**TBPA**$^{+\bullet}$ $SbCl_6^-$) (0.163 mg, 0.200 µmol). 3 Min after addition of oxidant the absorbance at 561 nm shifted to 550 nm. The spectral changes are due to $Cu^+$ translocation from $[Cu(\mathbf{1})]^+$ to **3** that result in a reorganisation of the switching arm from the zinc porphyrin to the phenanthroline station (black trace). The resulting solution was treated with decamethylferrocene (**dmfc**) (0.065 mg, 0.200 µmol). 3 Min after reduction the translocation of $Cu^+$ was completed because the absorption had fully changed from 550 to 561 nm indicating intramolecular docking of the azaterpyridine unit onto the zinc porphyrin (red trace).

**Analysis by ESI-MS**

Compounds **1** (220 µg, 201 µmol), **3** (365 µg, 201 µmol) and $[Cu(CH_3CN)_4]B(C_6F_5)_4$ (182 µg, 201 µmol) were dissolved in dry DCM. Then the solution was reacted with **TBPA**$^{+\bullet}$ $SbCl_6^-$ (164 µg, 201 µmol) and the resulting solution was divided into two parts. First part was characterised using ESI-MS (Figure S24) while the second part was reduced with **dmfc** (33.0 µg, 101 µmol). The reduced solution was analysed by ESI-MS as well (Figure S25).

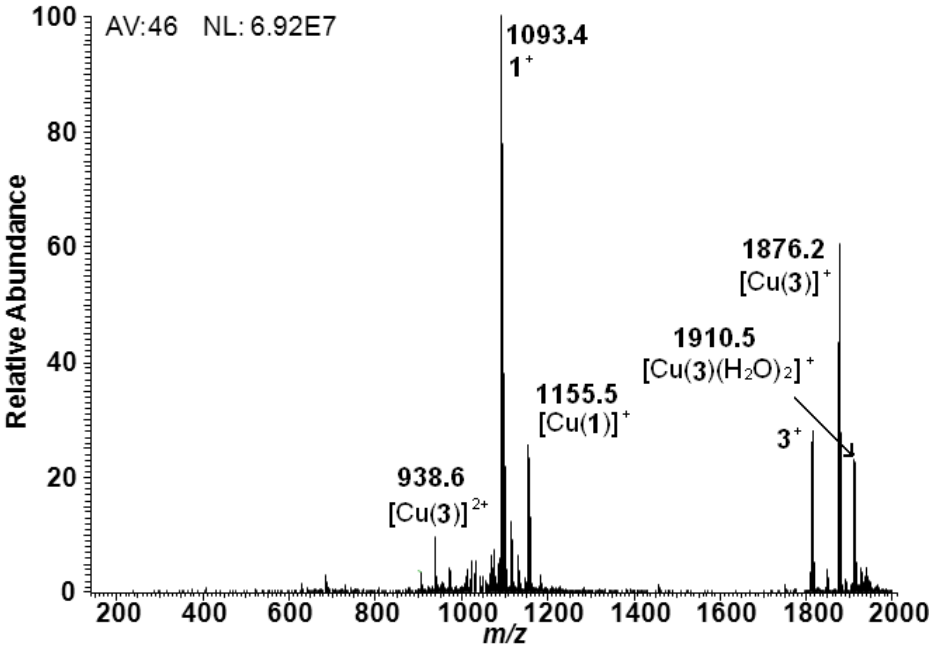



**Figure S24.** ESI-MS spectrum after oxidation of a solution of $[Cu(\mathbf{1})]^+$ and **3** in DCM with $\mathbf{TBPA}^{+\bullet}$ $SbCl_6^-$.

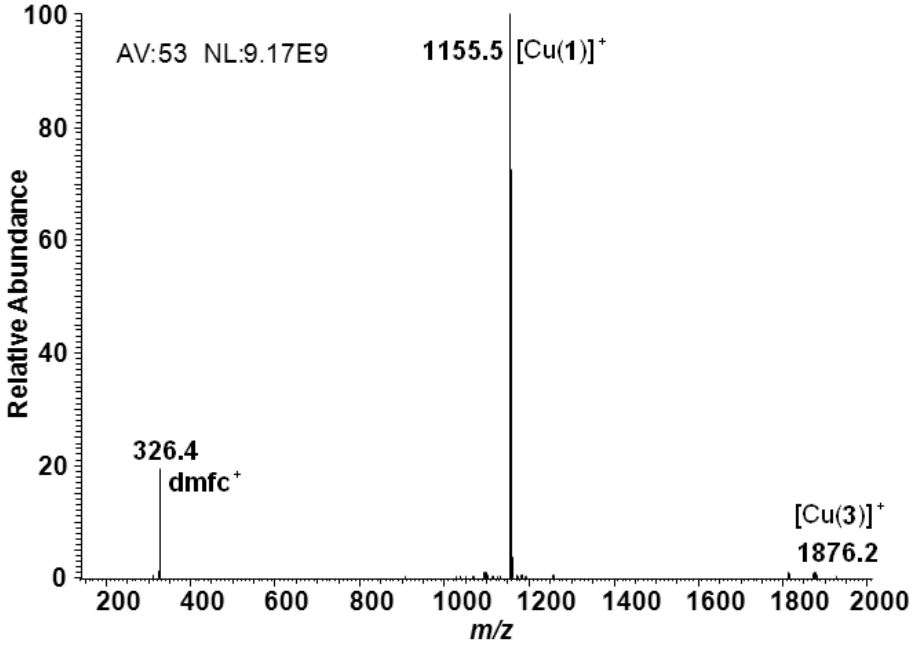



**Figure S25.** ESI-MS spectrum obtained after reduction of the above solution (Figure S24) with decamethylferrocene (**dmfc**) (33.0 μg, 101 μmol) in DCM.

## Communications between three switches

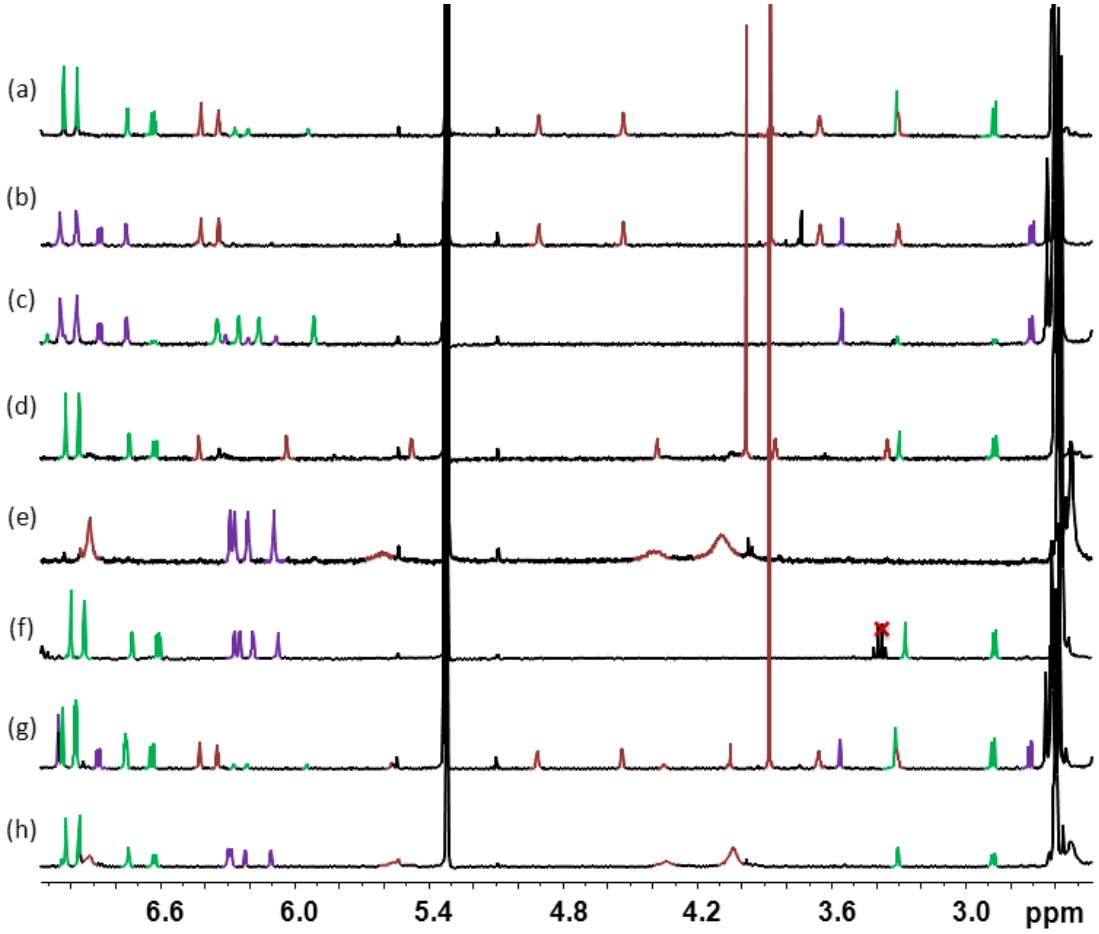



**Figure S26.** Partial $^{1}$H NMR spectra (400 MHz, $CD_2Cl_2$, 298 K) demonstrating the metal ion selectivity for the switches. The different traces represent: (a) formation of $[Cu(\mathbf{1})]^+$ and $[Cu(\mathbf{2})]^+$ (90:10) from a 1:1:1 mixture of **1**, **2** and $Cu^+$; (b) exclusive formation of $[Cu(\mathbf{1})]^+$ and free **3** in solution from a 1:1:1 mixture of **1**, **3** and $Cu^+$; (c) formation of $[Cu(\mathbf{2})]^+$ and $[Cu(\mathbf{3})]^+$ (90:10) from a 1:1:1 mixture of **2**, **3** and $Cu^+$; (d) exclusive formation of $[Zn(\mathbf{1})]^{2+}$ and free **2** in solution from a 1:1:1 mixture of **1**, **2** and $Zn^{2+}$; (e) exclusive formation of free **1** and $[Zn(\mathbf{3})]^{2+}$ from a 1:1:1 mixture of **1**, **3** and $Zn^{2+}$; (f) exclusive formation of $[Zn(\mathbf{3})]^{2+}$ and free **2** in solution from a 1:1:1 mixture of **2**, **3** and $Zn^{2+}$; (g) result after mixing **1**, **2**, **3** and $Cu^+$ showing 90% of $[Cu(\mathbf{1})]^+$ and 10% of $[Cu(\mathbf{2})]^+$ leaving **3** free in solution; (h) exclusive formation of $[Zn(\mathbf{3})]^{2+}$ when **1**, **2**, **3** and $Zn^{2+}$ (1:1:1:1) were mixed.

## $Cu^+$ translocation

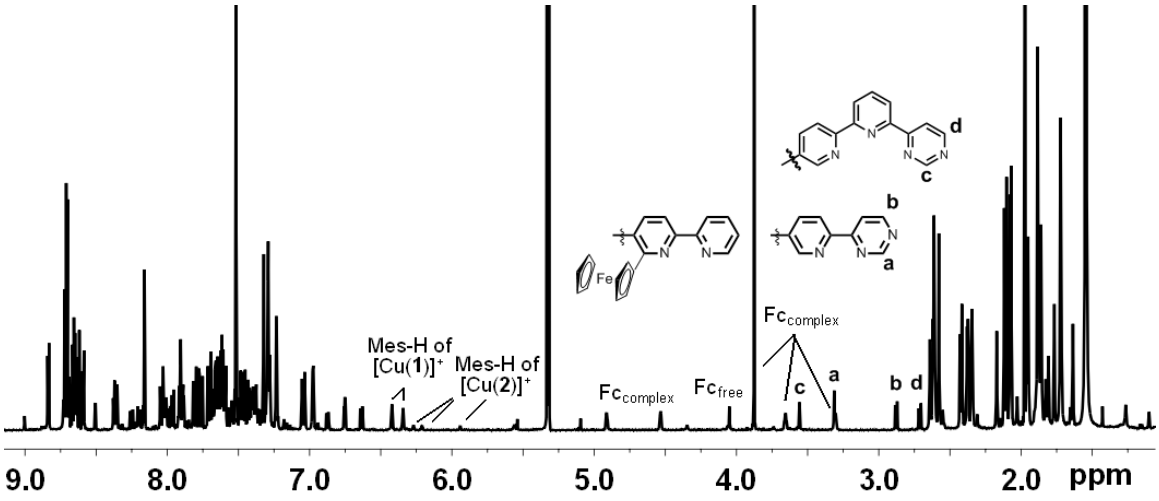



**Figure S27.** $^1$H NMR spectrum (400 MHz, $CD_2Cl_2$, 298 K) obtained after adding switch **2** (0.990 mg, 0.570 μmol) to a solution of [Cu(**3**)]$B(C_6F_5)_4$ (1.457 mg, 0.570 μmol) followed by addition of switch **1** (0.623 mg, 0.570 μmol) (0.71 mM). The spectrum shows a 90:10 ratio of $[Cu(\mathbf{1})]^+$ and $[Cu(\mathbf{2})]^+$ with switch **3** left free.

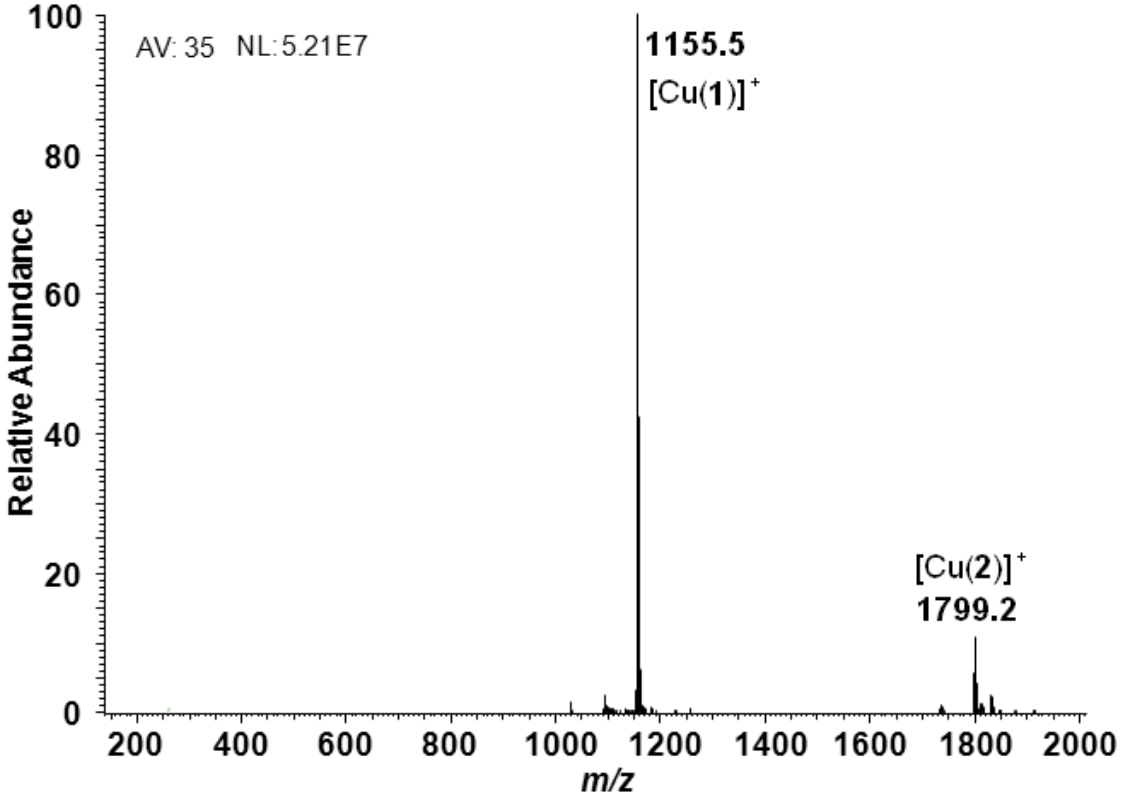



**Figure S28.** ESI-MS spectrum obtained from a mixture of **1**, **2**, **3** and $[Cu(CH_3CN)_4]B(C_6F_5)_4$ (1:1:1:1) in DCM.

## $Zn^{2+}$ translocation

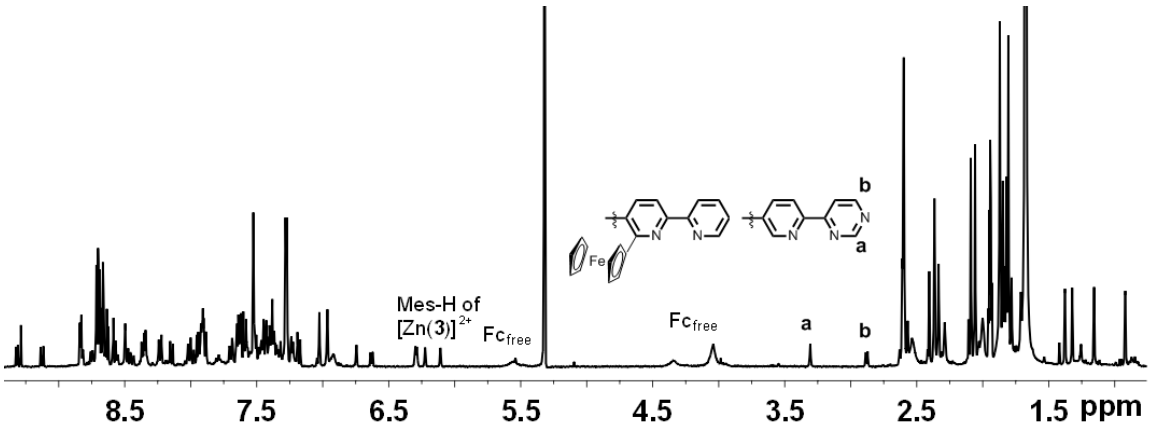



**Figure S29.** $^{1}$H NMR spectrum (400 MHz, $CD_2Cl_2$, 298 K) of a mixture of switches **1** (0.610 mg, 0.558 µmol), **2** (0.969 mg, 0.558 µmol), **3** (1.012 mg, 0.558 µmol) and $Zn(OTf)_2$ (0.203 mg, 0.558 µmol) (0.70 mM). The spectrum shows that $[Zn(\mathbf{3})]^{2+}$ is formed exclusively.

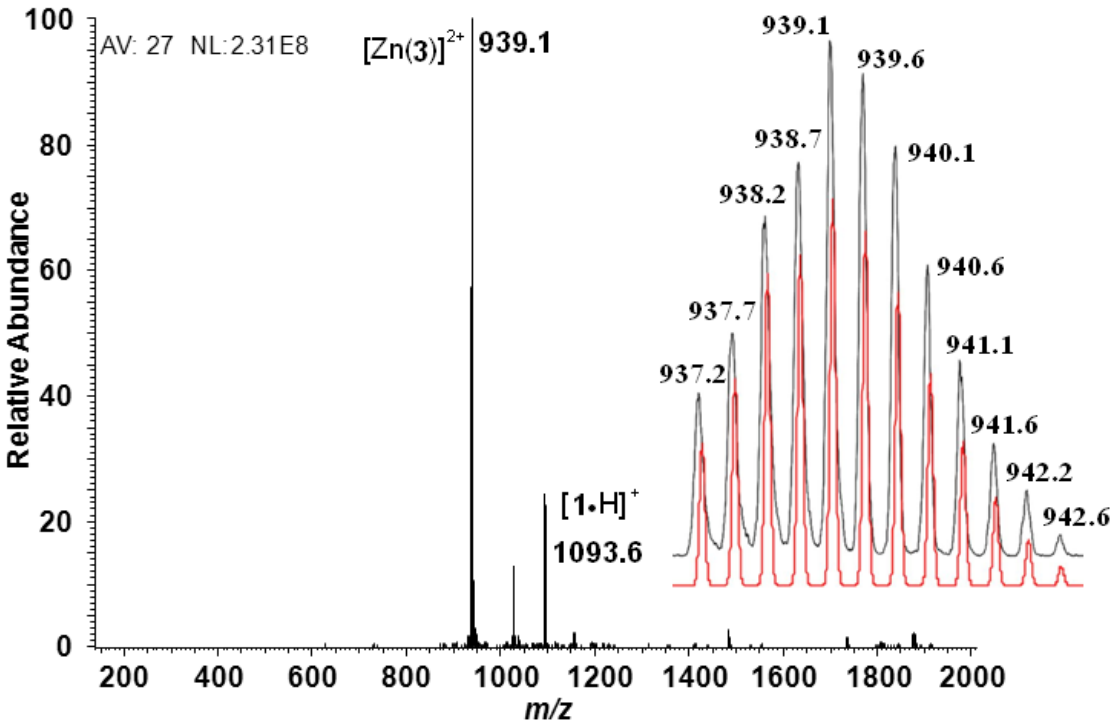



**Figure S30.** ESI-MS spectrum showing formation of only $[Zn(\mathbf{3})]^{2+}$ from a mixture of **1**, **2**, **3** and $Zn(OTf)_2$ in DCM.

## Reversible communication studies

### Forward communication

To check the forward communication, a solution of **1** (274 µg, 251 µmol), **2** (437 µg, 251 µmol), **3** (456 µg, 251 µmol) and $[Cu(CH_3CN)_4]B(C_6F_5)_4$ (227 µg, 251 µmol) in DCM was treated with **TBPA**$^{+\bullet}$ $SbCl_6^-$ (205 µg, 251 µmol). Then, the solution was divided into two parts. The first part was analysed by mass spectroscopy that clearly indicated $Cu^+$ translocation from $[Cu(\mathbf{1})]^+$ to switch **2** (Figure 31). The second part was again treated with another equiv. of the **TBPA**$^{+\bullet}SbCl_6^-$ (103 µg, 126 µmol). The ESI-MS spectrum recorded after the second oxidation suggested that $Cu^{2+}$ ions had translocated from $[Cu(\mathbf{2})]^+$ to switch **3** as seen by a peak at *m/z* = 938.6 Da (Figure 32).

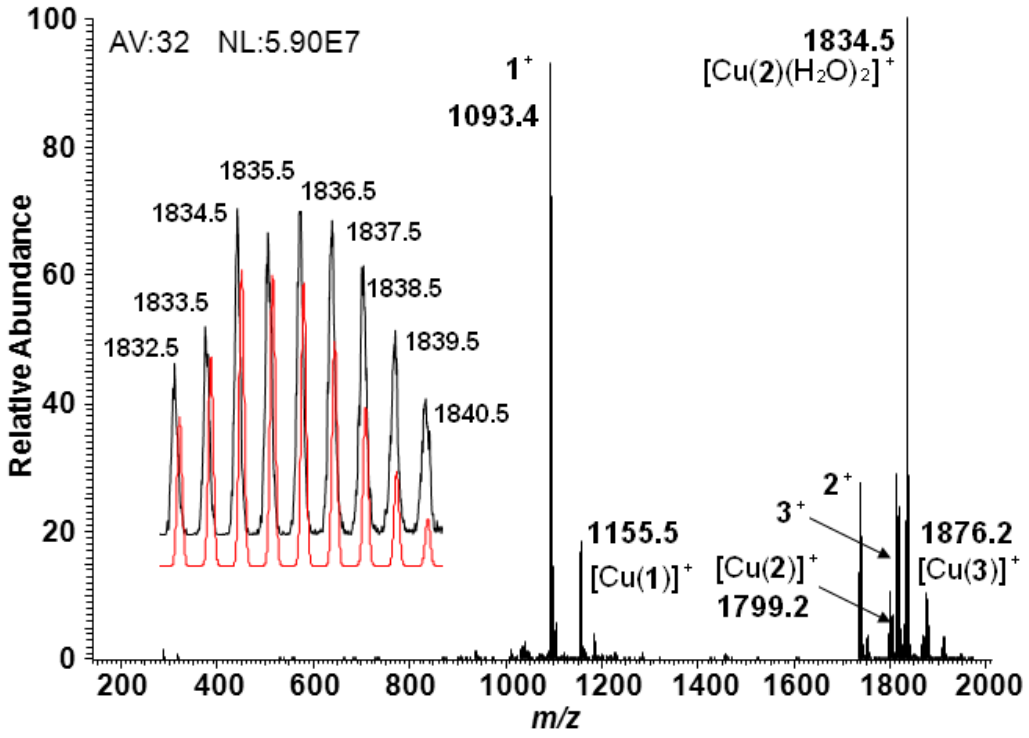



**Figure S31:** ESI-MS spectrum obtained after oxidation of a solution containing **1**, **2**, **3** and $Cu^+$ (1:1:1:1) by the first equivalent of **TBPA**$^{+\bullet}SbCl_6^-$.

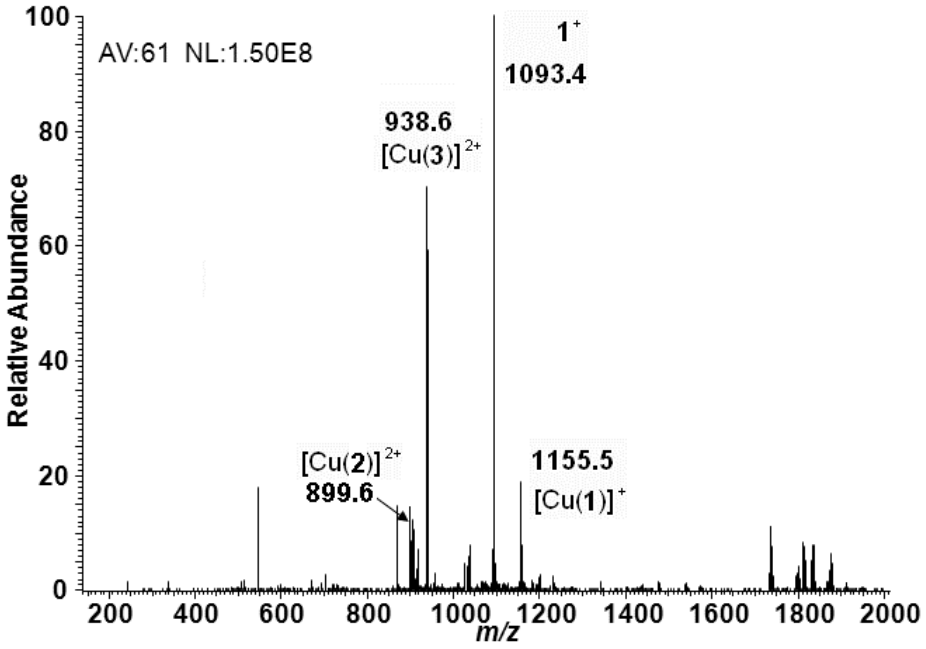



**Figure S32:** ESI-MS of the solution after second oxidation of the above solution (Figure 29) with another equivalent of **TBPA**$^{+\bullet}$$SbCl_6^-$.

## Backward communication

A mixture of **1** (317 µg, 290 µmol), **2** (504 µg, 290 µmol), **3** (526 µg, 290 µmol) and $[Cu(CH_3CN)_4]B(C_6F_5)_4$ (263 µg, 290 µmol) in DCM was treated with 2 equiv. of **TBPA**$^{+\bullet}$ $SbCl_6^-$ (473 µg, 580 µmol). Thereafter the mixture was treated with decamethylferrocene (0.095 mg, 290 µmol). The resulting solution was divided into two parts. The first part was analysed by ESI-MS (Figure 33) and UV-Vis. The second part was treated with decamethylferrocene (47.0 µg, 145 µmol) exhibiting formation of [Cu(**1**)]$^+$ and thus representing the start of the communication (Figure 34).

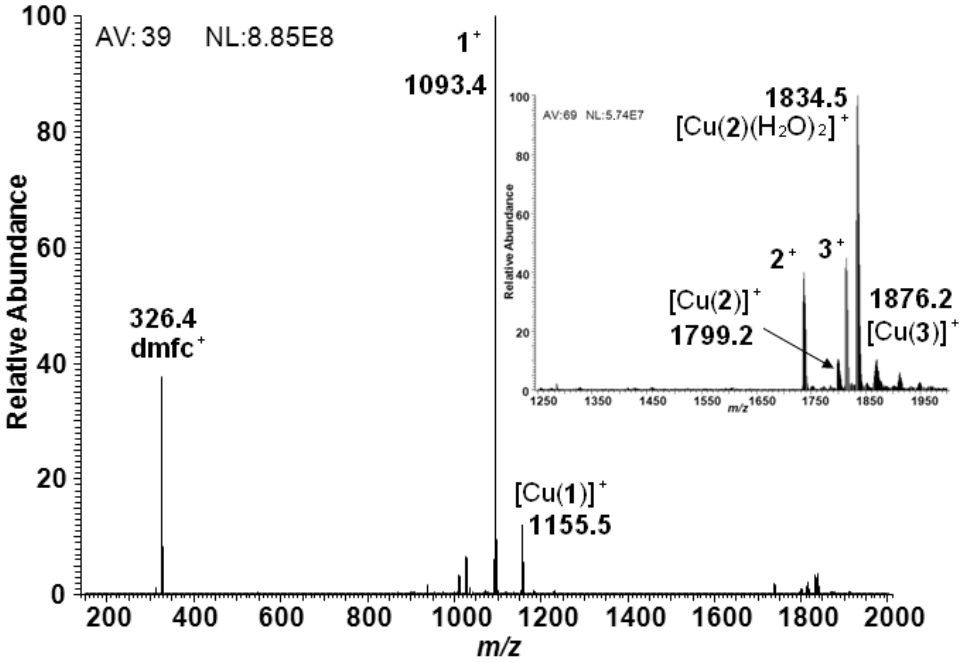



**Figure S33:** ESI-MS spectrum obtained after first reduction of a solution containing $\mathbf{1}^{+}$, **2** and $[Cu(\mathbf{3})]^{2+}$. The signals at 1834.5 and 1799.2 correspond to $[Cu(\mathbf{2})(H_2O)_2]^{+}$ & $[Cu(\mathbf{2})]^{+}$ and thus indicate some reduction of $Cu^{2+}$ and translocation of $Cu^{+}$ to switch **2**.

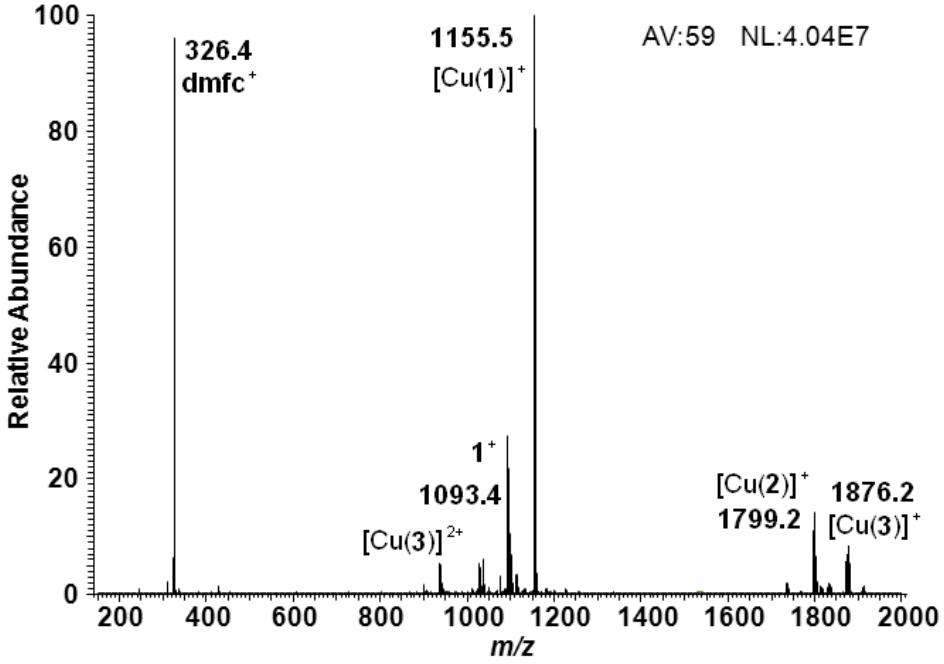



**Figure S34:** ESI-MS obtained after second reduction of the above solution from Figure S33 indicating full reset of the initial situation.

1. D. H. R. Barton, R. K. Haynes, G. Leclerc, P. D. Magnus and I. D. Menzies, *J. Chem. Soc., Perkin Trans. 1*, 1975, 2055.